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UCRL-PROC-217512

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December 5, 2005

Materials Research Society
Boston, MA, United States
November 28, 2005 through December 2, 2005

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Abstract

Plutonium, because of its radioactive nature, ages from the "inside out" by means of self-irradiation damage and thus produces nanoscale internal defects. The self-irradiation induced defects come in the form of Frenkel-type defects (vacancies and self-interstitial atoms), helium in-growth, and defect clusters. At present there are neither experimental nor theoretical models describing the changes in the electronic structure caused by the aging in Pu. This fact appears to be associated primarily with the absence of reasonably convincing spectroscopic evidence of the changes. This paper demonstrates that Resonant Photoemission, a variant of Photoelectron Spectroscopy, has strong sensitivity to aging of Pu samples. The spectroscopic results are correlated with an extra-atomic screening model [1], and are shown to be the fingerprint of mesoscopic or nanoscale internal damage in the Pu physical structure. This means that a spectroscopic signature of internal damage due to aging in Pu has been established.

Introduction

Plutonium is undoubtedly the most complex element in the periodic table. Notably, the pure metal exhibits six solid-state phases with large volume expansions and contractions along the way to the liquid state. Detailed understanding of the properties of plutonium and its alloys is critical for the science-based stockpile stewardship. The radioactive decay of plutonium represents another challenge to understanding this unique material. As a result of its radioactive nature, it undergoes self-irradiation damage throughout its volume, damaging its crystal lattice by generating Frenkel defects and transmuting some of the plutonium into other elements. Consequently, plutonium becomes even more complex as it ages. These damages lead to changes in the effective atomic volumes of the lattice. In most metals, such defects affect electronic properties. In plutonium, we also expect these changes because the 5f electrons sit on the knife-edge between bonding and localization. This paper demonstrates for the first time that Resonant Photoemission (RESPES), a variant of Photoelectron Spectroscopy, has strong sensitivity to aging of Pu samples.

Method and Results

The first experiments were performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley, CA [2]. The plutonium spectroscopy experiments were performed upon 2months old δ-Pu(Ga) and 10 years old δ-Pu(Ga)

samples. The sample surfaces were prepared by repeated room temperature, sputter-annealing cycles to minimize the oxygen and other impurities dissolved in the sample or at grain boundaries, in a specially designed chamber attached to the sample introduction and analysis chambers on Beamline 7.0. The transfer process from cleaning to the analysis chambers were always under vacuum, in order to minimize any surface contamination that could adversely affect the resonant photoemission. In fact, the oxygen 1s peak (BE = -529 eV) is not seen at wide photoemission scans at 1250 eV [2]. We estimate that the O/Pu concentration ratio to be approximately 6% [2].

The RESPES results for a young, highly purified δ-Pu(Ga) sample are compared with the corresponding measurements of an aged δ-Pu(Ga) in Figure 1. In this pseudo-three dimensional plots, the binding energy (0 to -12 eV) and photon energy (100 to 150 or 160 eV) are the in plane axes and intensity is the out of plane axis. To obtain this measurement, normalization is via flux measurements using a gold grid upstream from the photoemission site. Both young and aged samples exhibit the sigmoidal shape of RESPES. However, the aged sample appears to have a much more extended resonance range, with a high intensity at the Fermi Level extending out to photon energies of 150 eV, while the young sample has a significant drop in the intensity as the photon energy moves through 140 eV and higher. Comparing at specific photon energies, there is a consistent 20% to 30% amplification of the intensity near Fermi energy in the aged sample. While RESPES shows oxygen 2p peak (BE = -5 eV) in both samples, the oxygen contamination level is low and roughly comparable to the cleanest samples reported to data [2]. We estimate that the surface oxide to have negligible effect to the observed spectroscopic difference between young and aged samples. Furthermore, if the surface oxide did contribute to the resonant enhancement, we should see an equal enhancement in both young and aged samples. In contrast, we see much stronger enhancement in the aged sample than the young sample. Thus, the resonant enhancement in aged sample is from an age-driven effect.

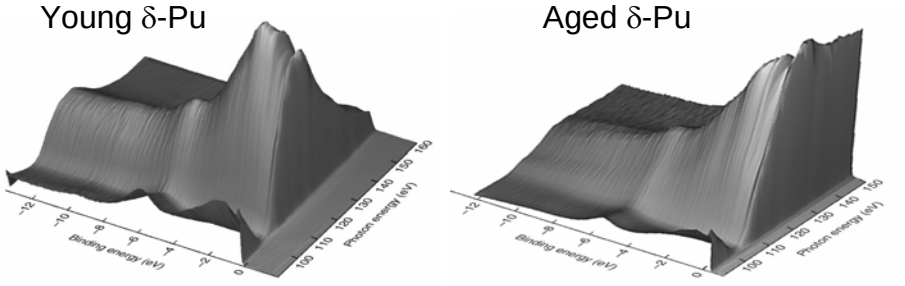

Figure 1. RESPES comparison between young and aged δ-Pu(Ga)[2].

The amplified RESPES effects in the aged δ-Pu(Ga) can be correlated with an extra-atomic screening model by Dowben [1]. In this model, if only intra-atomic decay is allowed, then there is only one possible decay process. However, if extra-atomic decay is allowed, then there are additional channels for decay. Based on the example of manganites [1], in its localized state (non-metallic), the single decay channel allows for the continued existence of the resonant behaviour. However, in its screened state

(metallic), the extra atomic decay channel quenches the resonant effect. This is essentially what has been observed in plutonium: the higher ordered young samples have superior screening, giving rise to a quenching relative to the aged samples. Because of the extended lattice disorder from the self-irradiation in the aged sample, the extra-atomic screening is compromised, allowing the amplified resonant behaviour relative to young samples.

Conclusion

We have shown age-dependent changes in the electronic structure of plutonium using resonant photoemission. Self-irradiation damage causes disorder in plutonium that leads to the resonant enhancement compared to higher ordered young plutonium. This analysis is founded upon a model of screening developed and experimentally tested by Dowben [1].

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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